

Bis (dibenzylidene acetone) palladium (0) catalyst for glycerol oxidation in half cell and in alkaline direct glycerol fuel cell

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ABSTRACT

In this study, catalytic activity and performance of bis (dibenzylidene acetone) palladium (0) catalyst, Pd (DBA)₂, was evaluated toward glycerol oxidation reaction (GOR) in alkaline half cell and alkaline direct glycerol fuel cell (DGFC). The electrooxidation of glycerol on Pd (DBA)₂ was characterized in half cell by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) techniques. Obtained results have highlighted the excellent electrocatalyst activity of Pd (DBA)₂ in terms of specific peak current density and onset potential compared to the results obtained by conventional Pd base catalysts. CVs results also demonstrate that Pd (DBA)₂ is still active even after 200 cycles.

In order to determine the performance of Pd $(DBA)_2$ in alkaline DGFC, membraneelectrode assembly was fabricated by employing the Pd $(DBA)_2$ catalyst in anode electrode, Acta commercial cathode and Tokuyama anion-exchange membrane and successfully evaluated in a single passive DGFC. Cell open circuit voltage and maximum power density of 800 mV and 24 mW cm⁻² were achieved, respectively by using static aqueous fuel containing 5 wt% of glycerol. Half and whole cell results exhibit acceptable activity and performance of Pd $(DBA)_2$ in GOR and suggesting it as a new promising anode catalyst for DGFC in alkaline media.

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1. Introduction

Development of alternative low temperature power source is an important and interesting subject for researchers in the world. Direct alcohol fuel cells (DAFCs) have attracted considerable interest in their application alternative power sources for portable consumer electronics and even automotives [1]. Among the different alcohols glycerol is an interesting candidate for DAFCs [2] because, it is much less volatile and less toxic (compared to methanol) and generated in large amounts during the production of both bio-ethanol and biodiesel [3–6]. Therefore, using glycerol as fuel in DAFCs is highly favorable in terms of safety, economic efficiency and environmental benefits.

Up to now, Pt-based catalysts are recognized as the best electrocatalyst for low temperature fuel cells [7]. However, the limitation of usage of Pt-based catalysts comes from high cost and limited resource of platinum [8]. Many efforts have been done for replacing of the Pt-based catalyst with Pd based catalyst specially in DAFCs because, it is at least fifty times more abundant in the earth [9] and less expensive than platinum. Notable works were carried out to assess the electrocatalytic behavior of supported and unsupported Pd electrocatalysts on glycerol and other alcohols oxidation

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[10-17]. All their results have shown that palladium is an active material for GOR especially in alkaline media. For example; Liang Su et al. [17] fabricated palladium/titanium dioxide (Pd/TiO₂) nanofibers and demonstrated the application of Pd/TiO₂ nanofibers for GOR in alkaline medium. Mario Simoes et al. [18] synthesized carbon supported Pd, Pt, Au and bimetallic PdAu and PdNi nano-catalysts and evaluated their catalytic activity toward GOR in alkaline medium. Their results showed that non-platinum based catalysts such as Pd_xAu_{1-x}/C and $Pd_{0.5}Ni_{0.5}/C$ have activity toward GOR close to the Pt/C catalyst. They found replacement of 50% of palladium atoms with nickel atoms leads to the improvement of the catalytic activity and in the same time to decrease the catalyst cost. In other studies, activities of oxide (CeO₂, NiO, Co₃O₄ and Mn₃O₄)-promoted Pd/C electrocatalysts have been studied in oxidation of alcohols. They also showed acceptable activity in alcohols oxidation in alkaline media [11]. Influence of the catalyst support on the activity of Pd for GOR was also studied by Z. Wang and V. Bambagioni et al. [10,12] in alkaline media.

The mechanism of electrochemical oxidation of glycerol on Pd in alkaline media is as follows;

Glycerol was converted to a plethora of species such as glyceraldehyde, glycerate, tartonate, glycolate, oxalate and CO_3^{-2} [12,18].

The oxidation processes of glycerol may undergo additional complicated reaction steps. This is because scission of more C–C and C–H bonds is necessary together with more efficient removals of intermediate species produced. Therefore, the oxidations not only depend on the activity of the respective catalyst for C–C and C–H bond breaking, but also, in particular, on its ability for oxidative removal of poisoning intermediates adsorbed.

A review on the activity of VIII group metals, it could be understood all zero-valent complexes with d^{10} electronic configurations have considerable catalytic interest toward alcohols oxidation [19]. One of the members of this series far less work has been done is Pd compared to Ni or Pt. This is due in part to the reduced stability of Pd (0) complexes and to the lower affinity of the Pd atom for Π -acceptor ligands which normally used to stabilize nucleophilic metal complexes [20].

In 1970 the synthesis of the useful air stable complex of bis (dibenzylidene acetone) palladium (0) was reported by Y. Takahashi et al. [21]. Synthesis of this complex is remarkably simple in contrast to other d^{10} group VIII metal complexes. The structure of Pd (DBA)₂ complex has been shown in Fig. 1. Pd (DBA)₂ is an extremely useful precursor to other Pd (0) complexes. Since the initial report of this work [21], various substitution and addition reactions have been reported along with an investigation of the potential utility of this complex as



Fig. 1 – Chemical structure of bis (dibenzylideneacetone) palladium (0), $Pd(DBA)_2$.

a catalyst [22]. Pd (DBA)₂ is strong nucleophile, strong base and most commonly used to catalyze reactions involving organic Halides, Acetates and Triflates. Recrystallization of Pd (DBA)₂ from various solvents affords novel binuclear palladium dibenzylidene acetone complexes of composition like Pd₂ (DBA)₃ [22]. Examples of reactions using this reagent are the Negishi coupling, Suzuki coupling, Carroll rearrangement, Trost asymmetric allylic alkylation, as well as Buchwald–Hartwig amination [22].

Full analysis of synthesis and characterization of the Pd $(DBA)_2$ and its similar compounds has been done in previous years by many researchers [21–25]. The catalytic properties of Pd $(DBA)_2$ in mentioned reactions make it potentially as a promising anode catalyst for alcohols oxidation in DAFCs.

According to our literature survey, no investigation has been done yet on employing of Pd (DBA)₂ as anode catalyst in DAFCs. In the present work, the activity of Pd (DBA)₂ catalyst has been investigated in electrooxidation of glycerol in alkaline medium by different electrochemical techniques such as; Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Chronoamperometry (CA). Finally, anode electrode has been made by Pd (DBA)₂ and successfully employed on first time in alkaline passive air breathing direct glycerol fuel cell.

2. Experimental

2.1. Electrochemical investigation

2.1.1. Deposition of Pd (DBA)₂ on glassy carbon

Bis (dibenzylideneacetone) palladium (0) (molecular weight of 575 g/mol, melting point 150 °C) was purchased from Sigma-–Aldrich Chemie GmbH. A thin film of catalyst layer on the glassy carbon electrode (with area of 0.0314 cm²) was prepared as follows: a mixture containing 2.0 mg electrocatalyst Pd (DBA)₂, 1 ml of 2-propanol (Merck), 1 ml of ultrapure water (MilliQ, Millipore, 18.2 MΩ-cm) and 0.01 ml of 5 wt% Nafion solution (Aldrich) was stirred ultrasonically for 5 min to obtain a well-dispersed ink. The catalyst ink was then quantitatively transferred onto the surface of the glassy carbon electrode by using micropipette, and finally dried in an oven at 60 °C for 15 min to remove the dispersion agent of the catalyst suspension. The catalyst loading on the electrode surface was 0.033 mg cm⁻².

2.1.2. CV, EIS and CA measurements

Half cell electrochemical measurements were carried out with a conventional three-electrode electrochemical cell and an Auto-lab PGSTAT30 potentiostat/galvanostat at 25 °C. The glassy carbon with the surface area of 0.0314 cm² was used as working electrode. A commercial Ag/AgCl electrode and Pt wire were also chosen as reference and counter electrode, respectively. All electrochemical measurements were carried out in the basic solution containing 10 wt% of KOH and 5 wt% of glycerol.

The electrochemical activity and stability of Pd (DBA)₂ in GOR were investigated by CV, EIS and CA techniques. CV was carried out by scanning of the potential between -0.7 and 0.4 V vs. Normal Hydrogen Electrode (NHE) with scan rate of

50 mV/s. EIS results were obtained at frequencies ranging between 100 kHz and 0.005 Hz by the amplitude of 10 mV at potential of 0 V vs. NHE. Chronoamperometry tests were also carried out at potential of Zero Volte vs. NHE.

All potential values in this article have been reported versus NHE.

2.2. DGFC preparation and evaluation

The anode electrode was made as follows: catalyst ink comprised of a homogeneous suspension of 95 wt% Pd (DBA)₂ catalyst with 5 wt% PTFE (Aldrich), isopropyl alcohol (Merck) and water. The ink was homogenized using a sonicator for 20 min and painted on nickel foam support as diffusion medium.

The cathode electrodes were prepared by painting the cathode ink on carbon cloth (LT2500W ELAT GDL from BASF) as diffusion medium. Cathode catalyst ink was prepared by mixing of 90 wt% Hypermec[™] K14 (Acta SpA) and 10 wt% PTFE and water as solvent according to reference [26]. Both electrodes were dried at 60 °C for 30 min in the oven. The total cathode and anode catalyst loading (containing catalyst and PTFE) were 3.5 and 5 mg/cm², respectively. The geometrical surface area of electrodes was 5 cm². The anode and cathode electrodes and A-006 Tokuyama anion-exchange membrane were sandwiched at room temperature in the cell hardware without using hot press. The MEA was placed in the airbreathing DGFC provided by Acta SpA.

The DGFC was tested by feeding static alkaline fuel containing 5 wt% glycerol and 10 wt% KOH in the anode side and static air in the cathode side. All tests were conducted on home-made test station at room temperature and ambient pressure. Polarization curve was recorded by measuring the cell voltage at different currents after reaching to steady state.

3. Results and discussion

0.80

3.1. Electrocatalytic activity and stability of Pd (DBA)₂

In order to study the intrinsic activity, leaching and stability of Pd (DBA)₂ in alkaline media, CV experiment was carried out in 1 M KOH solution. Fig. 2 indicates the corresponding cyclic



Fig. 2 – Cyclic voltammogram of Pd (DBA)₂ in 1 M KOH solution at room temperature with the scan rate of 50 mV/s.

voltammograms of 20th and 50th cycles of Pd (DBA)₂ in 1 M KOH solution at room temperature. Results indicate CV pattern of Pd (DBA)₂ is consistence with the CV patterns of palladium in alkaline media which have been reported in the literature [11–18,27]. As it can be seen in Fig. 2, the position and magnitude of the all peaks (forward and reverse scan) did not change in during 50 cycles, so catalyst did not leach to the solution.

Fig. 3 shows the cyclic voltammogram of the Pd (DBA)₂ in GOR in the solution containing 10 wt% of KOH and 5 wt% of glycerol. By considering of Fig. 2, glycerol oxidation peaks can be clearly observed in Fig. 3. The GOR on the surface of palladium catalyst is usually characterized by two well-defined current peaks on the forward and reverse scans [16]. In the forward scan, the forward anodic peak at ca. 0.08 V is corresponding to the oxidation freshly chemisorbed species coming from glycerol adsorption. The reverse anodic peak at -0.13 V is primarily associated with removal of carbonaceous species not completely oxidized in the forward scan than the oxidation of freshly chemisorbed species. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of palladium catalyst in glycerol oxidation reaction.

Table 1 indicates the relevant electrochemical parameters such as onset potential (E_s), forward anodic peak potential (E_p), peak current density (J_p) and specific peak current density (Sa_p) of Pd (DBA)₂ compared to typical GOR studies on platinum, palladium and palladium compound [10-12,18]. The performance of catalysts in GOR was evaluated in terms of two aspects: (1) onset potential (E_s) ; indicative of the catalytic activity over glycerol oxidation reactions, (2) forward anodic specific peak current density (Sa_p); showing the catalyst maximum performance. As it can be seen in Table 1, E_s and Sa_p value of Pd (DBA)₂ is respectively lower and higher value compared to what observed by oxides (CeO₂, NiO, Co₃O₄ and Mn₃O₄) promoted Pd/C, Pd/CPAA (Carbonized porous anodic alumina) and Pd/C in GOR roughly under the same conditions. E_s of Pd (DBA)₂ is 140 mV more negative than Pd/C in GOR. The specific current density of Pd (DBA)₂ is 0.48 mA/µg_{Pd} which is eight times higher than 0.06 mA/ μ g_{Pd} of Pd/C. These results



Fig. 3 – Cyclic voltammogram of Pd (DBA)₂ in the solution containing 10 wt% of KOH and 5 wt% of glycerol at room temperature with the scan rate of 50 mV/s.

Table 1 – Electrochemical activity of Pd(DBA)₂ compared to different electrocatalysts base on Pd and Pt in GOR in alkaline

media with the scan rate of 50 mV s $^{-1}$ at room temperature. (*E vs. RHE, sweep rate: 10 mV s $^-$ ¹). Pd loading J_p (mA cm⁻²) Electrocatalyst Solution (M) Eonset (V) Sa_{n} (mA/µg Pd) Ref. E_p (V) Gly/KOH (mg/cm^{-2}) [11] Pt/C 1/1 0.3 -0.38 0.03 21 0.07 Pd/C 1/1 0.3 0.19 18 0.06 [11] -0.19 Pd/C* 0.1/1(NaOH) 0.145 0.55 0.85 25 0.07 [18] 0.1/1(NaOH) 33 Pd_{0.5}Au_{0.5}/C* 0.065 0.45 0.88 0.09 [18] Pd-CeO₂ (1.3:1, w:w)/C 0.3 -0.23 0.05 50 0.16 [11] 1/1Pd-NiO (4:1, w:w)/ C 1/1 0.3 -0.22 0.07 88 0.29 [11] Pd-Co₃O₄ (2:1, w:w)/C 1/1 0.3 -0.28 0.05 70 0.23 [11] Pd-Mn₃O₄ (2:1, w:w)/C 1/1 03 -0.290.12 65 0.21 [11] Pd/MWCNT 5wt%/2 0.017 0.12 2.8 [12] -0.453.7

-0.3

-0.33

-0.1

0.08

70

16



1/1

1/2

0.3

0.03

Fig. 4 – Cyclic voltammograms (1th, 30th, 70th, 100th, 140th, 170th and 200th cycle) of Pd (DBA)₂ in the solution containing 10 wt% of KOH and 5 wt% of glycerol at room temperature with the scan rate of 50 mV/s.

demonstrate that Pd (DBA)₂ has significantly higher activity than oxides (CeO₂, NiO, Co₃O₄ and Mn₃O₄) promoted Pd/C, Pd/CPAA and Pd/C, but lower activity than Pt/C and Pd/MWCNT (multi-walled carbon nano-tube).

0.23

0.48

[10]

Current study

In order to study the tolerate of Pd $(DBA)_2$ against GOR intermediate products 200 of CV was also recorded in the solution containing 10 wt% of KOH and 5 wt% of glycerol. Fig. 4 shows the cyclic voltammograms (1 ft, 30th, 70th, 100th, 140th, 170th and 200th cycle) of Pd $(DBA)_2$ with the scan rate of 50 mV/s in the potential range of -0.7 to 0.4 V. As it can be seen the anodic peak current of the electrode clearly increases with increasing of scan number during the initial stages and then this trend in the growth of the peak currents declines with further increasing of the scan number. Improvement of the peak current during the initial stage probably results from the catalyst activation. The subsequent decline in the peak current of glycerol oxidation is due to catalyst poisoning by GOR intermediate products. As it described in Scheme 1,



Scheme 1 – Glycerol oxidation mechanism on the surface of Pd in alkaline media.

Pd/CPAA

Pd (DBA)₂

intermediates products have different active functions which can adsorb on the surface of catalyst and reduce catalyst active surface area. It causes a reduction in the peak current of glycerol oxidation during CV cycles.

The highest peak current for electrode arises during the 60th cycle scan. After this cycle the peak current decreases slowly with successive scans. After 200 CV cycles the glycerol oxidation current declines by approximately 33% as it could be understood from the Fig. 2. The reverse anodic peak current density still exists even after 200 cycles. This results show Pd (DBA)₂ is active in GOR even after 200 cycles which can be explained by high tolerate and stability of Pd (DBA)₂ catalyst against poisoning by GOR intermediate products.

3.2. EIS study Pd (DBA)₂ in GOR

Fig. 5 indicates the nyquest plots of GOR on the Pd $(DBA)_2$ catalyst in the solution containing 10 wt% KOH and 5 wt% glycerol at the constant potential of 0 V, after 1 ft and 200th cycle. There is a pronounced arc followed by a diagonal line in both EIS curves. The arc corresponds to the RC model of the activation kinetics and the diameter of the loop gives activation resistance. At the initial cycle nyquest plot shows a smaller value for charge transfer resistance (R_{ct}) but by increasing the number of cycles R_{ct} increases dramatically as it can be observed in 200th cycle. A possible explanation is that by increasing the cycle number, Pd (DBA)₂ is poisoned by glycerol oxidation byproducts and intermediates and so R_{ct} has been increased after 200th cycle. These results are consistence with CVs results which plotted in Fig. 4.

The diagonal line at low frequencies is due to mass transport as modeled by the infinite Warburg impedance. From the frequency-impedance data of this line, the mass transport properties can be extracted.

3.3. Chronoamperometry study of Pd (DBA)₂ in GOR

Fig. 6 shows typical chronoamperograms (before getting CV and after 50th, 100th, 150th and 200th CV cycles) of glycerol oxidation on the Pd (DBA)₂ in the solution containing 10 wt% of KOH and 5 wt% of glycerol at potential of 0 V versus NHE. All



Fig. 5 – Nyquest plots of Pd (DBA)₂ catalyst after the cyclic voltammograms 1 ft and 200th cycle in the solution containing 10 wt% of KOH and 5 wt% of glycerol at potential of 0 V.



Fig. 6 – Chronoamperograms (before getting CV and after 50th, 100th, 150th and 200th CV cycle) of Pd $(DBA)_2$ catalyst in the solution containing 10 wt% of KOH and 5 wt% of glycerol at room temperature, applied potential: 0 V.

of the curves displayed the decay of current during the time which could be related to the remaining of the adsorbed intermediate products of glycerol oxidation on the surface of catalyst. As it is shown, the current density of Pd (DBA)₂ catalyst to 50th cycle behaved with a more gently decreasing trend because the activation of catalyst occurred as it described before(section 3.1). The attenuation behavior of electrode after 50th cycle is determined by the coverage of intermediates and glycerol adsorbed on the catalyst active sites.

3.4. DGFC performance

According to the electrochemical results which were conducted in previous sections Pd $(DBA)_2$ has comparable activity in the glycerol oxidation reaction compared to literature data, so examination of mentioned catalyst in the anode side of alkaline DGFC is reasonable. The test result of MEA made by Pd $(DBA)_2$ anode catalyst in alkaline passive air breathing DGFC has been reported in Fig. 7. Cell temperature was 25 °C



Fig. 7 – I–V and power density curves of alkaline passive air-breathing DGFC made by Pd (DBA)₂ anode catalyst with the fuel containing 10 wt% of KOH and 5 wt% of glycerol at room temperature.

Table 2 – Comparison of reported passive/active DGFCs performance in the literature.								
DGFC	Gas breathing	Anode	Cathode	Membrane	Solution (KOH/Glycerol)	MPD (mW/cm ⁻²)	T (°C)	Ref.
Passive	02	Pd/MWCNT (3.8%)	Fe–Co hypermec K-14	Tokuyama A-006	2 M, 5wt%	6	20	[12]
Active	O ₂ (200 mL min ⁻¹)	Pd/MWCNT (3.8%)	Fe—Co hypermec K-14	Tokuyama A-006	2 M, 5wt% (4 mL min ⁻¹)	16	25	[12]
Active	O_2 (200 mL min ⁻¹)	Pd-(Ni—Zn)/C	Fe—Co hypermec K-14	Tokuyama A-006	2 M, 5wt% (4 mL min ⁻¹)	16	25	[28]
_	O ₂	Pt/C	Pt/C	ADP	2 M/4 M	4.2	25	[30]
_	O ₂	Pd/C	Pt/C	ADP	2 M/4 M	2.4	25	[30]
_	O ₂	Au/C	Pt/C	ADP	2 M/4 M	1	25	[30]
_	O ₂	AuPd/C	Pt/C	ADP	2 M/4 M	0.3	25	[30]
Active	O ₂ (40 mL min ⁻¹)	Pt/C (40%)	Pt/C	Fumapem [®] FAA fumatech	1 M/4 M	8	25	[29]
Active	O_2 (40 mL min ⁻¹)	Pt ₉ B ₁ /C, (40%)	Pt/C	Fumapem [®] FAA fumatech	1 M/4 M	10	25	[29]
Passive	Air	Pd (DBA) ₂	Fe—Co hypermec K-14	Tokuyama A-006	2 M, 5wt%	24	25	Current study

and cell was fed by static fuel containing 10 wt% of KOH and 5 wt% of glycerol. From a perusal of this figure, one readily realizes that the open circuit voltage and maximum power density are 800 mV and 24 mW cm⁻², respectively. High mass transport issue in high current density region could be attributed to the not optimized electrode structure and thus it means electrode optimizations are required for higher current density. Table 2 indicates maximum power density of the Pd (DBA)₂ compared to active and passive alkaline DGFCs performance reported in the literature [12,28–30]. A review of this table shows that firstly, Pd (DBA)₂ could be a good candidate for alkaline DGFC and secondly, identical or even higher performance can be obtained by the anode made by Pd (DBA)₂ catalyst.

However for deeper understanding of Pd $(DBA)_2$ activity and stability in alkaline DGFC under different conditions much more investigations have to be done in future.

4. Conclusions

In this work, bis (dibenzylidene acetone) palladium (0), Pd (DBA)₂, was employed as an effective catalyst for glycerol electrooxidation in alkaline media. The activity, leaching and stability of Pd (DBA)₂ catalyst in GOR were investigated in half cell with different electrochemical techniques. Obtained results have highlighted the excellent electrocatalyst activity of Pd (DBA)₂ in terms of specific peak current density and onset potential. Test results demonstrated that Pd (DBA)₂ is still active and stable even after 200 cycles.

Membrane-electrode assembly (MEA) was made by Pd (DBA)₂ catalyst in the anode side and commercial Hypermec[™] cathode catalyst in the cathode side and Tokuyama A-006 anion-exchange membrane as electrolyte and successfully evaluated in alkaline passive air breathing DGFC. By considering the cell peak power density (24 mW/cm²) obtained at room temperature with static fuel and air breathing condition, one can safely conclude that Pd (DBA)₂ exhibits acceptable

activity for glycerol oxidation in the anode side for alkaline DGFC application.

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